

CHEMICAL COMPOSITION AND PROCESS

The present invention relates to a composition and a process for de-inking of recycling paper, and a process for preparation of the composition.

Recycling paper has become an increasingly important raw material for production of paper, both for economic and environmental reasons. When the recycling paper includes printed waste paper, such as newspapers or journals, de-inking is normally necessary. A conventional de-inking process includes adding a soap solution or a melted fatty acid to an alkaline aqueous fibre stock suspension from recycling paper, optionally together with other chemicals, and followed by removal of ink particles, for example by flotation. In order to achieve effective de-inking, it is important that the soap or fatty acid is rapidly emulsified or dispersed into the fibre stock suspension.

CA Patent Application 2147384 discusses certain draw-backs of these methods and discloses a de-inking process comprising treating a slurry of wastepaper with a composition comprising a fatty acid and a non-ionic surfactant.

US Patent 4483742 discloses a liquid soap for use in paper re-cycling comprising a fatty acid saponified to about 50%.

However, none of the above methods give a fully satisfactory result in respect of brightness and/or fibre losses.

US Patent 4586982 discloses an improved de-inking process comprising adding a fatty acid or a resinic acid to a suspension of wastepaper fibres in the form of a previously prepared aqueous emulsion or dispersion.

Use of pre-prepared emulsions or dispersions as described above generally gives fully satisfactory de-inking, but requires transport of the entire composition, including the water, from the supplier to the pulp mill. Further, emulsions and dispersions are complicated to prepare and may suffer from low storage stability and sensitivity to both low and high temperatures.

It is an object of the invention to provide a solid fatty acid composition for de-inking that either can be added directly to a fibre suspension or in a simple manner be transformed to an aqueous emulsion or dispersion on-site by mixing it with water.

It is another object of the invention to provide a solid fatty acid composition for de-inking that is simple to prepare.

It is still another object of the invention to provide a process for de-inking of recycling paper that results in both high brightness and low fibre losses.

It has surprisingly been found that these object can be achieved by a product and a process according to the appended claims.

More specifically, the invention concerns a solid composition for de-inking of recycling paper comprising at least one fatty acid that is partially saponified with at least one alkaline substance. Suitably the degree of saponification is from about 1 to about 90%, preferably from about 1 to about 50%, most preferably from about 1 to about 30% particularly most preferably from about 2 to about 10%. The degree of saponification

refers to the saponified portion of the total number of saponifiable carboxylic groups in the fatty acid or fatty acid mixture. It is assumed that substantially all of the alkaline substance used participates in the saponification. The total content of partially saponified fatty acids is suitably from about 50 to 100 wt%, preferably from about 70 to 100 wt%, most preferably from about 85 to 100 wt%.

The product is suitably in the form of a powder, granules, flakes or the like, preferably with a particle size from about 0.1 mm to about 10 mm, most preferably from about 0.5 mm to about 5 mm.

It has been found that totally non-saponified fatty acids, even in liquid form, are difficult to disperse uniformly into an aqueous fibre stock suspension, which results in poor de-inking. It is also difficult and time consuming to pre-prepare a dispersion thereof before adding it to the fibre stock suspension. On the other hand, totally saponified fatty acids tend to gel, particularly at low temperatures (e.g. at room temperature), which also results in poor de-inking.

According to the invention, it has been found that the novel composition forms emulsions or dispersions more rapidly than non-saponified fatty acids, but does not gel as easily as totally saponified fatty acids do. It is thereby possible to add the product of the invention directly to an aqueous fiber stock suspension and still achieve satisfactory de-inking. If it is desirable to add the product as an emulsion or dispersion, this can be prepared much easier than from a non-saponified fatty acid.

Without being bound to any theory, it is believed that the saponified part of the at least one fatty acid acts as a dispersant, rendering the composition to be self-emulsifying or self-dispersing.

The at least one fatty acid is selected from those that in partially saponified state are solid at room temperature (about 20-25°C). Preferred fatty acids have from 8 to 24, preferably 14 to 20 carbon atoms, and preferably have from 0 to 3 double bonds. Examples of such fatty acids are myristic acid, palmitic acid, stearic acid, arachidic acid and behenic acid, and mixtures thereof. Particularly preferred are palmitic, stearic, and arachidic acid, and mixtures thereof. It is in most cases preferred to use mixtures of different fatty acids, which mixtures normally are commercially available.

The alkaline substance may be selected from inorganic or organic compounds. Inorganic compounds include, for example, ammonia or hydroxides and carbonates of alkali metals and alkaline earth metals, such as sodium, potassium or calcium, alone or in mixtures. Organic compounds are most preferred and may, for example, include various organic amines, alone or in mixtures. One suitable group of amines have the general formula $R_1R_2R_3N$, where R_1 - R_3 , independently of each other, can be hydrogen, alkyl groups, aryl groups, hydroxyalkyl groups or other organic substituents, wherein it is preferred that at least one of R_1 - R_3 is an organic substituent. Particularly preferred amino compounds include amino alcohols such as ethanol amines and propanol amines.

Monoethanol amine (MEA), diethanol amine (DEA) and triethanol amine (TEA), and mixtures thereof, are most preferred.

Although the composition may comprise more than 96 wt% or even substantially consist of at least one saponified fatty acid, it can further include additives conventionally used in de-inking like at least one dispersant (in addition to the saponified part of the at least one fatty acid), alkali metal silicate, one or several cellulosic derivatives, one or several complexing agents, one or several oxidative bleaching agents, or inert substances such as one or several fillers.

If one or more dispersants are present, which in some cases can be advantageous, the total content thereof is suitably from 0 up to about 30 wt%, preferably from about 2 to about 15 wt% (not including the saponified part of the at least one fatty acid). Dispersants may be selected from non-ionic, an-ionic, cat-ionic and amphoteric surfactants, among which non-ionic surfactants are preferred. Suitable non-ionic surfactants include alkoxylated compounds preferably having from 14 to 20 carbon atoms, such as fatty alcohols, acids, alkylphenols, alkylamines, mono- di- and triglycerides, and alkyl polyglycosides or polyhydroxy fatty acid amides, alone or in mixtures. Particularly preferred surfactants are ethoxylated and/or propoxylated compounds, preferably having from 4 to 120 ethylene oxide units and/or from 4 to 40 propylene oxide units.

Alkali metal silicate, preferably metasilicate, of sodium, potassium or a mixture thereof, may, for example, be present in an amount from 0 up to about 5 wt%, preferably from about 0.5 to about 3 wt%. The alkali metal silicate serves the purpose of chelating heavy metal ions such as copper, chromium, iron, manganese and the like, that catalyses decomposition of peroxides present during the de-inking but also in stabilising loosened printing ink against redepositing on the fibres during the de-inking. Further, alkali metal silicate may also contribute to saponification of the fatty acid in the composition.

If one or more cellulose derivatives are present, the total content thereof is suitably from 0 up to about 1 wt%, preferably from about 0.1 to about 0.5 wt%. Cellulose derivatives may, for example, be selected from carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl methyl cellulose, ethyl hydroxyethyl cellulose or mixtures thereof. Cellulose derivatives serve the purpose of preventing small ink particles from redepositing on the fibres during the de-inking.

If one or more complexing agents are present, the total content thereof is suitably from 0 up to about 2 wt%, preferably from about 0.1 to about 1.0 wt%. Complexing agents may, for example, be selected from EDTA, DTPA, phosphonic acids and salts or other derivatives thereof, or mixtures thereof. Complexing agents serve the purpose of chelating heavy metal ions such as copper, chromium, iron, manganese and the like, that catalyses decomposition of peroxides present during the de-inking.

If one or more oxidative bleaching agents are present, the total content thereof is suitably from 0 up to about 3 wt%, preferably from about 0.5 to about 2 wt%. Oxidative bleaching agents may, for example, be selected from solid substances generating

peroxides, preferably hydrogen peroxide, in aqueous solutions. Such solid substances include, for example, alkali metal salts of percarbonate, perborate, peroxyulfate, peroxyphosphate or peroxyasilicate.

- If one or more fillers are present, the total content thereof is suitably from 0 up to about 10 wt%, preferably from about 1,0 to about 4 wt%. Fillers may, for example, be selected from talc, calcium carbonate, different kinds of clays etc.

In addition to the above mentioned components, the composition of the invention may also include any substance that otherwise would be possible to add separately in a de-inking process or substances improving the physical properties of the composition.

- The invention also concerns a process for preparing a composition as described above comprising a step of mixing at least one fatty acid with at least one alkaline substance and any optional components to be included, preferably at a temperature from about 10 to about 40°C, most preferably from about 15 to about 25°C. The at least one alkaline substance is added in an amount sufficient to obtain a desirable degree of saponification. If the at least one alkaline substance is solid, the components are preferably mixed in a solid state. If the at least one alkaline substance is liquid, the fatty acid is preferably added in melted form, whereupon the mixture is cooled to obtain a solid product, to which any optional component can be added. The solid mixture can then be ground and sieved or treated in any other suitable way to obtain a powder, granules, flakes or the like with a desired particle size. Compared to fatty acid dispersions and emulsions that earlier have been used for de-inking, the product of the invention can be prepared in a very simple manner. However, it is also possible to prepare the composition by first making an aqueous dispersion or emulsion of at least one fatty acid and at least one dispersing agent, partially saponifying said at least one fatty acid by adding at least one alkaline substance, before or after the dispersion or emulsion is prepared, and then drying, for example spray drying, the dispersion or emulsion to yield a solid product.

- The invention further concerns a process for de-inking of recycling paper, using the composition of the invention as described above, suitably in an amount from about 0.01 to about 5 wt%, preferably from about 0.05 to about 1 wt%, most preferably from about 0.1 to about 0.5 wt% based on the recycling paper.

- In one embodiment, the process comprises the steps of preparing an aqueous fatty acid emulsion or dispersion from water and a solid composition of the invention as described above, and adding the obtained emulsion or dispersion to the recycling paper or to the water forming an aqueous fibre stock suspension thereof. The fatty acid emulsion or dispersion can be prepared with moderate mixing energy and at a comparatively low temperature, preferably from about 25 to about 90°C, most preferably from about 30 to about 50°C, but still result in an emulsion or dispersion with excellent physical properties, e.g. small particle size (preferably from about 0.1 to about 10 µm, most preferably from about 0.5 to about 2.0 µm) and high liquidity and stability. When

using this dispersion or emulsion it is easy to achieve rapid distribution of the fatty acid in the fibre stock suspension and thereby also good de-inking.

In another embodiment, the process comprises a step of adding the solid composition of the invention directly to the recycling paper or to the water forming an aqueous fibre stock suspension thereof. It has been found possible to disperse or emulsify the solid composition directly into the fibre stock suspension, and thereby getting away from the extra step of first preparing an emulsion or dispersion of the fatty acid. If the composition is packed in containers of paper, such as bags, sacks or boxes of paper, the entire containers can be added to the recycling paper or the fibre stock suspension, thereby avoiding dusting problems. Furthermore, the paper in the container may include components active in the de-inking process or a following pulping process.

The aqueous fibre stock suspension may be prepared by any conventional means from recycling paper such as newspapers, magazines, office waste and the like to a preferred dry content from about 2 to about 30 wt%, most preferably from about 4 to about 20 wt%. Apart from the at least one fatty acid included in a composition of the invention, in solid, emulsified or dispersed form as described above, it is preferred to add to the recycling paper or the fibre stock suspension one or more other conventional de-inking chemicals, separately and/or included in a composition of the invention. Such conventional de-inking chemicals include one or several dispersants, alkali metal silicate, one or several cellulose derivatives, one or several complexing agents, and one or several oxidative bleaching agents. Examples of such de-inking chemicals are given in the above description of the composition, although they of course also may be added in liquid form, for example as aqueous solutions. The oxidative bleaching agent is preferably added as an aqueous hydrogen peroxide solution. Furthermore, it is preferred to add separately one or more alkaline substances such as alkali metal hydroxide, preferably sodium hydroxide, to obtain a suitable pH of the fibre stock suspension. This pH is preferably from about 7 to about 12, most preferably from about 8 to about 10, under which conditions the added fatty acid or acids become substantially completely saponified and to some extent, together with calcium, magnesium or other polyvalent metal ions, precipitate and form flakes or other kinds of aggregates. After a suitable time, preferably from about 2 min to about 100 min, most preferably from about 10 to about 30 min, at a suitable temperature, preferably from about 10 to about 90°C, most preferably from about 30 to about 75°C, and preferably under moderate agitation, most of the ink particles have been detached from the fibres and deposited on the precipitated saponified fatty acid. The ink particles may then be removed by any conventional means, for example by flotation and/or washing, and the remaining de-inked fibre stock suspension be used for making paper.

The order of the addition of the chemicals is not critical, and the composition of the invention may be added, as a solid material or a dispersion or emulsion thereof, to the recycling paper or to the water before or after the fibre stock suspension is formed and

before or after other chemicals are added. Further, it is also possible not to add any oxidative bleaching agent until after the removal of the ink particles.

Some embodiments of the invention will now be described in connection with the following Examples which, however, not should be interpreted to limit the scope of the invention. If not otherwise stated, all parts and percentages refer to parts and percents by weight.

Example 1: Fifteen solid compositions were prepared by various combinations from the following ingredients:

FA = Mixture of C_8 - C_{24} fatty acids, mainly C_{18} and C_{18} , Iodine number $< 3 \text{ mg I}_2 \text{ per } 100 \text{ g}$ fatty acid mixture, Saponification number 205 mg/g ; OA = Oleic acid; TEA = triethanol amine; P 4000 = polyethylene glycol 4000 g/mole ; HPMC = hydroxypropyl methyl cellulose; EHEC = ethyl hydroxyethyl cellulose; FAC 25 = C_{18-18} fatty acid alkoxyated with 25 moles of ethylene oxide/propylene oxide 70/30; Fac 50 = C_{18-18} fatty acid alkoxyated with 50 moles of ethylene oxide/propylene oxide 70/30; FAI 120 = C_{18-20} fatty alcohol alkoxyated with 120 moles of ethylene oxide/propylene oxide 70/30; EPE = ethylene oxide propylene oxide block polymer; FAI 4 = C_{9-11} fatty alcohol ethoxyated with 4 moles of ethylene oxide; PC = sodium percarbonate; MS = sodium metasilicate; CC = calcium carbonate; KOH = potassium hydroxide; Talc = talcum powder.

The compositions in wt% are specified in Table 1, which also gives the degree of saponification (DS) in %.

Compositions No. 1-7 were prepared by grinding the ingredients together in a laboratory mill followed by sieving through a 1 mm screen. The material $>1\text{mm}$ was milled again to pass the 1 mm screen. Compositions No. 8 and 9 were prepared by mixing the liquid ingredients with the fatty acid in its molten form. The products were then ground and sieved as compositions No. 1-7. Compositions No. 10 and 11 were prepared by mixing compositions No. 8 and 9, respectively, with the other ingredients, followed by grinding and sieving as described above. Compositions No. 12-15 were prepared by mixing the liquid ingredients with molten fatty acids. The solid materials obtained after cooling were then flaked.

Solid compositions were also prepared by spray drying the commercially available fatty acid dispersions Ecollect™ 5030 and 5230 (Eka Chemicals AB, Sweden), which both are 30% dispersions in water of mostly saturated fatty acids and surfactants with a pH of 5-9 and a viscosity lower than 300 mPas .

Table 1

Comp. No.	FA	OA	TEA	P4000	HPMC	EHEC	PC	MS	CC	KOH	Talc	FAc25	FAc50	FAH20	EPE	FAH4	DS
1	88.18			5.01	0.30		5.01			0.50	1.00						3
2	84.13			4.81			4.81	0.96		0.48	4.81						3
3	75.00			10.00			5.00	2.00	4.00	1.00	3.00						7
4	80.00			10.00			5.00	2.00		1.00	2.00						6
5	80.00			5.00			8.00	2.00	2.00	1.00	2.00						6
6	80.00			15.00				2.00		1.00	2.00						6
7	81.83			9.98		0.20	4.99	2.00		1.00		10.00					6
8	80.00	5.00	1.00											4.00			2
9	80.00	5.00	1.00										10.00	4.00			2
10	75.12	4.70	0.94			0.10	2.00	2.00		2.00	2.00	9.39		3.76			2
11	75.12	4.70	0.94			0.10	2.00	2.00		2.00			9.39	3.76			2
12	98.00		1.00														2
13	95.00		5.00														10
14	90.00		10.00														20
15	89.10		2.10												6.20	2.60	4

Example 2: The compositions prepared in Example 1 were used to prepare aqueous dispersions. Compositions No. 1-7, partially saponified with KOH, could be made into 15% dispersions in 75-80°C water, using an Ultra Turrax mixer at 3000 rpm. Compositions No. 8-15, partially saponified with TEA, could be made into 15% dispersions at lower temperature, 35-40°C, with lower stirring energy, using a laboratory mixer at 800 rpm. This yielded dispersions with small particles and liquid dispersion at room temperature.

Example 3: In four sets of trials the compositions No. 1-15 and the spray dried dispersions of Example 1 were tested for deinking waste paper in a pulper. The compositions were added in dry (i.e. solid) form and/or as dispersions prepared according to Example 2.

Water of 45°C and 6°dH and the following chemicals were added to a Hobart mixer: 0.5% of sodium hydroxide, 1.0% of water glass, 0.7% of hydrogen peroxide and 0.12% of one of the deinking compositions of the invention or 0.12%, calculated as solid, of the liquid commercial product Ecollect™ 5230 as a reference. Waste paper, 70% newspapers and 30% magazines, was added to the water and chemicals mixture to get a waste paper consistency (concentration of suspended solids) in the pulper of 15%. All additions of chemicals are in per cent by weight calculated on the waste paper.

The mixture was stirred for 15 minutes and then transferred to a Lamort type laboratory flotation cell and diluted with water of 45°C and 6°dH to 1 % consistency. The flotation was then started and samples were taken out before flotation and after 12 min of flotation. The amount of solid substance lost in the flotation was determined. The pH was measured in the 15% pulp suspension and in the 1% suspension before flotation and after the flotation, and in all the experiments determined to be between about 8.6 to 9.4. The pulp samples from 0 and 12 min of flotation were made into sheets. The brightness, as % reflectance at 457 nm, was determined on these sheets. The Effective Residual Ink Concentration, ERIC, was also measured on the sheets from 0 and 12 min flotation time. The principle for the ERIC measurement is to use an infrared radiation of 950 nm to measure the amount of fragmented printing ink in a paper sample.

The results from each set of trials are summarised in Tables 2-5, showing that using a composition of the invention, either in solid form or as a pre-dispersed fatty acid dispersion, give about the same or even better effect in deinking than the commercial fatty acid dispersion Ecollect 5230 used as a reference.

Table 2

Product (Comp. No.)	Ref. Ecollet 5230	4 disp.	4 dry	5 disp.	5 dry	6 disp.	6 dry	7 disp.	7 dry	8 dry	9 dry	10 disp.	10 dry	11 disp.	11 dry
Brightness (%ISO); 0 min	43.2	44.6	43.9	43.9	44.0	44.1	44.1	43.3	44.3	42.9	43.5	42.8	45.0	44.5	43.2
Brightness (%ISO); 12 min	52.4	54.1	52.1	53.2	51.2	53.2	52.7	53.4	53.9	53.2	55.3	52.8	52.6	53.4	54.0
Brightness increase 0-12 min	9.2	9.5	8.2	9.3	7.2	9.1	8.6	10.1	9.6	10.3	11.8	10.0	7.6	8.9	10.8
ERIC (ppm); 0 min	1095	1008	1055	1038	1033	1045	1067	1081	1058	1099	1068	1131	1034	1054	1078
ERIC (ppm); 12 min	411	390	428	397	451	436	457	390	404	409	304	409	431	384	376
ERIC decrease 0-12 min	684	628	627	641	582	609	610	701	654	690	764	722	603	670	702
pH 15%	9.3	9.3	9.3	9.3	9.3	9.3	9.2	9.3	9.3	9.3	9.3	9.4	9.2	9.3	9.2
pH 1% before flotation	9.1	9.1	9.1	9.0	9.1	9.0	9.1	9.1	9.1	9.1	9.0	9.1	9.0	9.1	9.0
pH 1% after flotation	9.1	9.0	9.0	8.8	9.1	9.0	9.0	9.0	9.0	9.1	9.0	9.0	9.0	9.0	9.0
Total losses	8.8	7.1	7.3	2.2	7.1	6.3	5.4	6.8	7.6	7.3	8.2	9.2	6.7	8.6	6.5
Solids losses	7.6	6.9	6.7	2.5	6.8	6.2	5.6	6.9	6.7	7.3	8.2	8.2	6.3	7.5	7.5

Table 3

Product (Comp. No.)	Ref. Ecollect 5230	12	13	14	15
Brightness (%ISO); 0 min	51.2	50.1	49.8	49.8	49.4
Brightness (%ISO); 12 min	55.6	56.9	55.9	55.8	55.8
Brightness increase 0-12 min	4.4	6.8	6.1	6.0	6.4
ERIC (ppm) ; 0 min	686	748	747	721	803
ERIC (ppm) ; 12 min	326	311	343	341	349
ERIC decrease 0-12 min	360	437	404	380	454
pH 15%	9.1	9.2	9.3	9.2	9.3
pH 1% before flotation	8.9	9.0	9.0	9.0	9.1
pH 1% after flotation	8.7	8.9	9.0	9.0	9.0
Solids losses	6.3	6.9	6.2	6.1	6.6

Table 4

Product	Reference 1 Ecollect 5230	Comp. No 1 dispersion	Comp. No. 2 dispersion	Comp. No. 3 dispersion
Brightness (%ISO); 0 min	47.0	47.8	47.8	46.6
Brightness (%ISO); 12 min	52.7	52.6	52.0	52.4
Brightness increase 0-12 min	5.7	4.8	4.2	5.8
ERIC (ppm) ; 0 min	798	765	857	776
ERIC (ppm) ; 12 min	212	301	495	357
ERIC decrease 0-12 min	586	464	362	419
pH 15%	9.1	9.2	9.2	9.3
pH 1% before flotation	8.8	8.8	8.9	9.0
pH 1% after flotation	8.6	8.7	8.7	8.8
Total losses	1.9	2.3	2.9	2.2
Solids losses	2.2	2.8	2.3	2.5

Table 5

Product	30% Ecollect 5030	Dried Ecollect 5030	30% Ecollect 5230	Dried Ecollect 5230
Brightness (%ISO); 0 min	37.6	37.3	36.3	36.5
Brightness (%ISO); 15 min	44.2	44.3	45.7	45.9
Brightness increase 0-15 min	6.6	7.0	9.4	9.4
Water brightness (%ISO); 15 min	59.0	61	65.7	68.3
Solids losses	8.1	8.2	7.9	7.6

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